present in large groups of MS. Figures 6 and 12 in particular provide a kind of summary of the information present in the MS of the isomers of $C_{10}H_{14}$.

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Application of Alkali Ions in Chemical Ionization Mass Spectrometry

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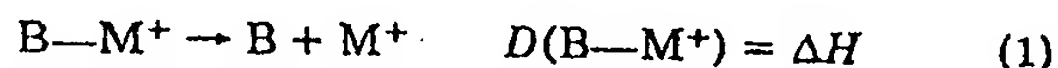
A technique is described for obtaining mass spectra consisting solely of quasi-molecular ions formed by addition of an alkali ion to the sample molecule. Alkali ions are generated by thermionic emission externally to the enclosed ion source and injected into a reagent gas containing a trace amount of sample. Alkali ions initially bind to the reagent molecules and then are transferred to the sample in bimolecular reactions. Experimental conditions, choice of a reagent gas, and potential applications are discussed.

Chemical ionization (CI) mass spectrometry (1) is a form of mass spectrometry in which the sample is ionized in ion–molecule reactions with reagent ions. The sample is introduced into the mass spectrometer as a trace component in a reagent gas. The reagent ions are usually produced by electron impact ionization and ion–molecule reactions in the reagent gas.

Generally CI mass spectra contain few ions and often exhibit major molecular or quasi-molecular ions, thus giving the molecular weight of the substance. This is particularly useful in cases where the electron impact mass spectrum does not yield a molecular ion. An effective method to avoid fragmentation and produce a quasi-molecular ion is to bind a relatively inert reagent ion to the neutral sample molecule. For example, when $Si(CH_3)_4$ is used as a reagent gas, the principal reagent ion formed is $Si(CH_3)_3^+$. This ion forms addition complexes with representative compounds containing a range of functional groups to give the abundant quasi-molecular ion $(P + 73)^+$ (2). Halide ions, which can be generated conveniently from appropriate reagent gases in dissociative attachment processes, bind to a variety of functional groups under CI conditions to give the quasi-molecular ion $(P + X)^-$ (3, 4). Recent studies have demonstrated similar behavior for alkali cations (5–10). The use of alkali ions as reagent species for CI mass spectrometry has not, however, been previously explored. We report studies which delineate the experimental conditions and suggest applications for using alkali ions as reagent species in CI mass spectrometry.

The binding energy of a Lewis base, B, to an alkali ion, M^+, is defined by the enthalpy change for Equation 1.

$$B\text{—}M^+ \rightarrow B + M^+ \qquad D(B\text{—}M^+) = \Delta H \qquad (1)$$

Values for the enthalpy, entropy and free energy changes in Equation 1 for B = H_2O and Ar are listed in Table I. The enthalpy and free energy changes decrease monotonically in proceeding from Li^+ to Cs^+. In the columns labeled $p(H_2O)$ and $p(Ar)$ are listed the pressure of H_2O and Ar at which the equilibrium ratio $[B\text{–}M^+]/[M^+]$ is unity at 298 K. Clearly, the binding energy of the reagent ion to the sample molecule is an important consideration in choosing a reagent ion. The binding energy must be great enough to permit a significant stable population of the complex at the partial pressure of the species being analyzed. It is evident from the data in Table I that Li^+ is the preferred alkali ion reagent for trace analysis. Using Li^+ to detect a species with a partial pressure of 10^{-7} Torr in a sample at 10^{-1} Torr (1 ppm), it is desirable to have an enthalpy of binding in excess of 21 kcal/mol. This assumes a typical entropy change of 20 eu for Equation 1.
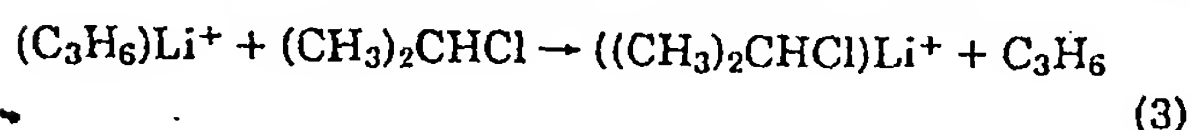
Recently, complexes of alkali ions with Lewis bases have been generated and studied using the techniques of ion cyclotron resonance spectroscopy (6–8). These complexes are formed in bimolecular reactions of Li^+ and Na^+ with certain alkyl halides. For example, Li^+ reacts with isopropyl
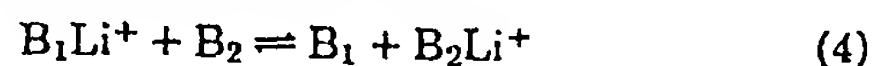
Table I. Thermodynamic Data for the Process B—M⁺ → M⁺ + B

Table I. Thermodynamic Data for the Process $B{-}M^+ \rightarrow M^+ + B$

M	B = H₂O[a]				B = Ar			
	$\Delta H°^b$	$\Delta S°^c$	$\Delta G°^b$	$p(H_2O)^d$	$\Delta H°^{b,c}$	$\Delta S°^{c,f}$	$\Delta G°^{b,f}$	$p(Ar)^d$
Li⁺	34.0	23.0	25.5	1.5×10^{-16}	5.8	15.7	1.1	120
Na⁺	24.0	21.5	17.6	9.4×10^{-11}	3.9	14.3	−0.4	1500
K⁺	17.9	21.6	11.4	3.3×10^{-6}	2.5	13.8	−1.6	1.1×10^4
Rb⁺	15.9	21.2	9.6	6.9×10^{-5}	...			
Cs⁺	13.7	19.4	7.9	1.2×10^{-3}	2.1			

[a] Reference 5. [b] Kcal/mol. [c] eu. [d] $p(B)$ is the pressure of B in Torr at which the equilibrium ratio $[B{-}M^+]/[M^+]$ is unity at 298 K, $p(B) = 760 \exp(-\Delta G/RT)$. [e] Reference 10. [f] Calculated value.

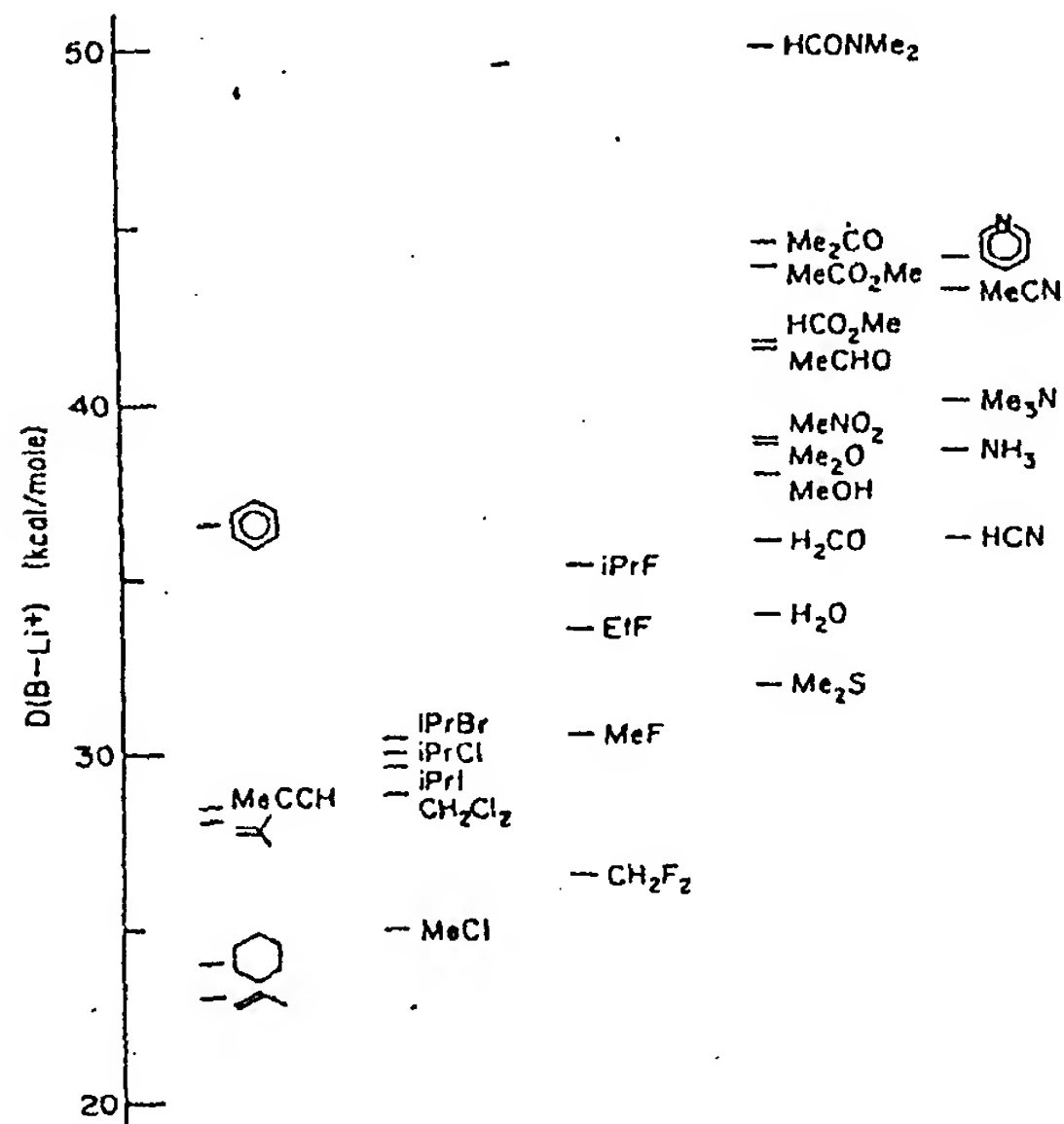chloride to form the complex of Li^+ with propylene (Equation 2).

$$Li^+ + (CH_3)_2CHCl \rightarrow (C_3H_6)Li^+ + HCl \quad (2)$$

$$(C_3H_6)Li^+ + (CH_3)_2CHCl \rightarrow ((CH_3)_2CHCl)Li^+ + C_3H_6 \quad (3)$$

This complex reacts rapidly to transfer Li^+ to $(CH_3)_2CHCl$ (Equation 3). When other gases are added, transfer of Li^+ between molecules (Equation 4) leads to the formation of other complexes of Li^+ with n-donor, π-donor, and even σ-donor bases such as cyclohexane (7).

$$B_1Li^+ + B_2 \rightleftharpoons B_1 + B_2Li^+ \quad (4)$$

The enthalpy change for a reaction involving transfer of an ion between molecules is a measure of the relative binding energy of the ion to the molecules. The relative binding energies of several molecules toward Li^+ have been determined by trapped ion cyclotron resonance techniques (7). A scale of Li^+ binding energies (Figure 1) has been constructed by combining the results of these determinations and is referenced to the experimental (5) and theoretical (11–14) value for $D(H_2O{-}Li^+) = 34$ kcal/mol. These data indicate that a wide range of compounds have sufficient Li^+ binding energies to be detectable at low concentrations.

Figure 1. Binding energies of molecules to Li⁺ (data from Ref. 7)

EXPERIMENTAL

An ion source, consisting of a thermionic alkali ion emitter (15), a reaction chamber and appropriate electrostatic lenses, was constructed (Figure 2). The ion source is contained in a 6-in. o.d. housing, which is pumped by a 4-in. diffusion pump. The ions are mass analyzed and detected by an EAI Quad 250B quadrupole mass spectrometer, which is connected to the source housing through a 1.5-in. port and is differentially pumped by a 50 l. sec⁻¹ ion pump.

Sample gas is admitted into the chamber through a Granville-Phillips leak valve. The pressure in the chamber is monitored by an MKS Instruments Baratron Model 90H1 capacitance manometer. The pumping capacity and reaction chamber apertures limit the maximum chamber pressure to 50 mTorr.

The alkali ion emitter is a small mineral bead (about 1-mm diameter) fused to 0.007-in. diameter rhenium filament wire. The mineral β-eucryptite, used for thermionic generation of Li^+, is prepared by direct application of a hand torch to a thoroughly ground mixture of $LiOH:Al_2O_3:SiO_2$ in a 1:1:1 molar ratio. Filament wire is dipped into the melt to achieve the desired coating. A current of 2 A through the filament is sufficient to produce an ion emission current of 10^{-6} A. Under these operating conditions the lifetime of a filament is over 100 h. For the first few hours of operation, emission of the contaminants Na^+ and K^+ may be significant. These subsequently decrease to less than 0.1% of the total emission. The emission characteristics may be profoundly affected by exposure to gases during filament operation and reactions may occur on the filament which give rise to complexes of Li^+ with small molecules. Consequently, the filament must be mounted externally to the reaction chamber. The distance from the filament to the chamber is 2.5 cm in the present apparatus.

Potentials to the source elements are supplied by potentiometric circuits. The elements are all cylindrically symmetrical with circular apertures. An immersion lens (Figure 2) accelerates the ions and forms them into a beam. The beam travels through a field-free region and is then decelerated to the desired energy between the
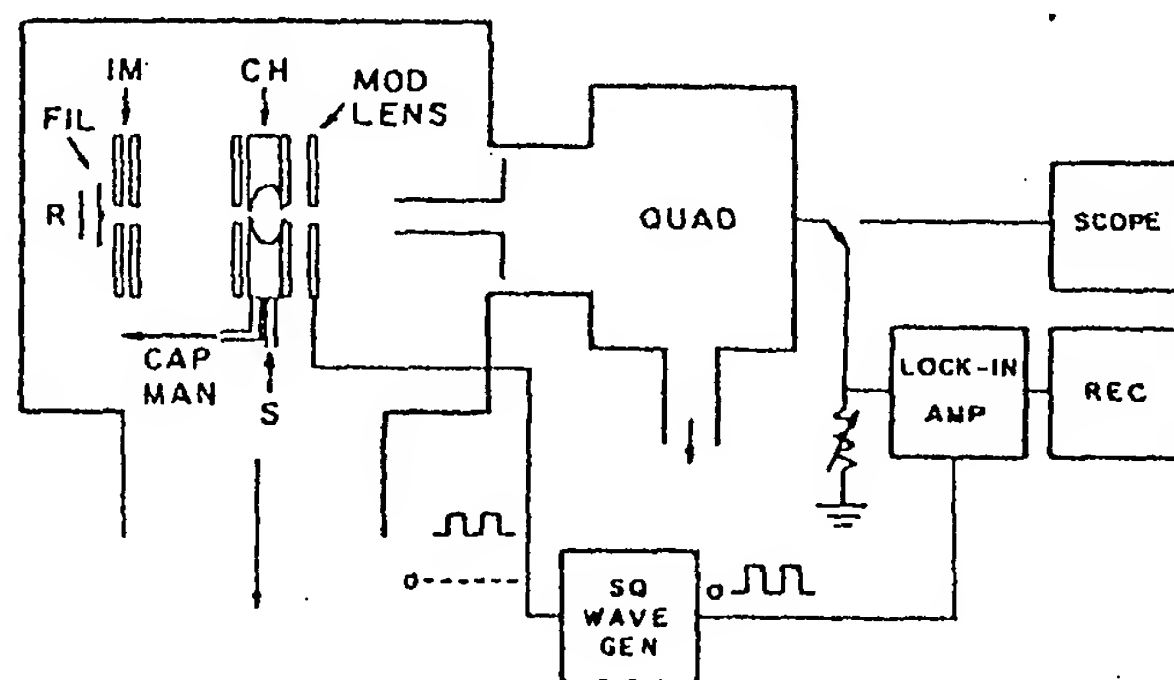

Figure 2. Schematic of the ion source, mass spectrometer, and detection electronics

R, repeller plate; FIL, filament; IM, immersion lens; CH, reaction chamber; S, sample gas inlet; CAP MAN, outlet to capacitance manometer; MOD LENS, modulating lens; QUAD, quadrupole mass spectrometer; REC, recorder; SQ WAVE GEN, square wave generator

third lens element, and the reaction chamber. The entrance aperture of the chamber is 1 mm in diameter. The chamber was constructed with axial, rather than perpendicular, symmetry, since the former gives greater sensitivity. The chamber is composed of two electrically insulated parts so that an extraction potential can be placed across the chamber. The internal shape of the chamber is due to Werner (16) and is designed to create an efficient extracting field. Product ions and unreacted alkali ions exit the chamber through a 1.5-mm diameter orifice and are focused by a final lens element into the quadrupole mass spectrometer.

An acceptable signal-to-noise ratio is achieved through the use of phase sensitive detection. The signal is modulated by applying a square wave to the final lens element. The output of the channeltron electron multiplier can be observed on an oscilloscope or detected using a PAR HR-8 lock-in amplifier, referenced to the modulating frequency. The output of the lock-in amplifier is recorded on a strip chart recorder.

The ion intensities were not corrected for the mass discrimination of the quadrupole mass spectrometer.

RESULTS

General Considerations. A successful method for obtaining Li^+ CI mass spectra must provide a means for binding Li^+ to the sample molecules. For the analysis of mixtures, the sensitivity of the method should be reasonably constant regardless of the nature of the sample constituents. Fragmentation and clustering processes, which produce additional ions in the spectrum, should be minimal. The sample must be present at low partial pressure or examined at low conversion to avoid Li^+ transfer reactions between sample molecules, which would result in an increase in the abundance of the Li^+ complex with the species of highest Li^+ binding energy.

Two approaches to the binding of Li^+ to the sample may be envisioned. Li^+ can be injected into a relatively inert gas, such as N_2, that contains a trace amount of sample, and Li^+–sample complexes are formed by termolecular association reactions. Since termolecular association reaction rate constants vary widely depending primarily on the number of atoms in the product cluster (17, 18), the sensitivity of this technique will vary widely. For example, the rate constant for the termolecular association of Li^+ with C_2H_3Br is 8.4×10^{-27} molecule^{-2} cm^6 sec^{-1}, compared to a rate constant of 1.6×10^{-29} molecule^{-2} cm^6 sec^{-1} for the association of Li^+ and CO_2 (18). Another disadvantage is that some sample compounds, such as alkyl halides, undergo exothermic bimolecular reactions with Li^+ (e.g., Equation 2), which produce species other than quasi-molecular ions.

Alternatively, the sample can be present as a minor constituent in or added to a gas, which itself binds Li^+. The Li^+–reagent gas complex is formed either by a termolecular association reaction or a bimolecular sequence, such as Equations 2 and 3, depending on the nature of the reagent gas. These complexes then transfer Li^+ to the sample molecules, in analogy with more conventional CI experiments (1), in which reagent ions are generated in situ. The rate constants for exothermic Li^+ transfer reactions are expected to fall between 0.8×10^{-9} and 2×10^{-9} cm^3 molecule^{-1} sec^{-1}, with the faster rates corresponding to processes involving polar neutrals (19). This limited range stems from the fact that the rates of exothermic bimolecular ion–molecule reactions are largely determined by long range interactions between the ion and neutral species (19, 20). Consequently, the sensitivity of this method toward different molecules is expected to be relatively constant in comparison to the sensitivity when the Li^+ complexes are formed in association reactions.

The choice of an appropriate reagent gas is governed by several considerations. 1) The reagent gas must have a lower Li^+ binding energy than any of the sample molecules,
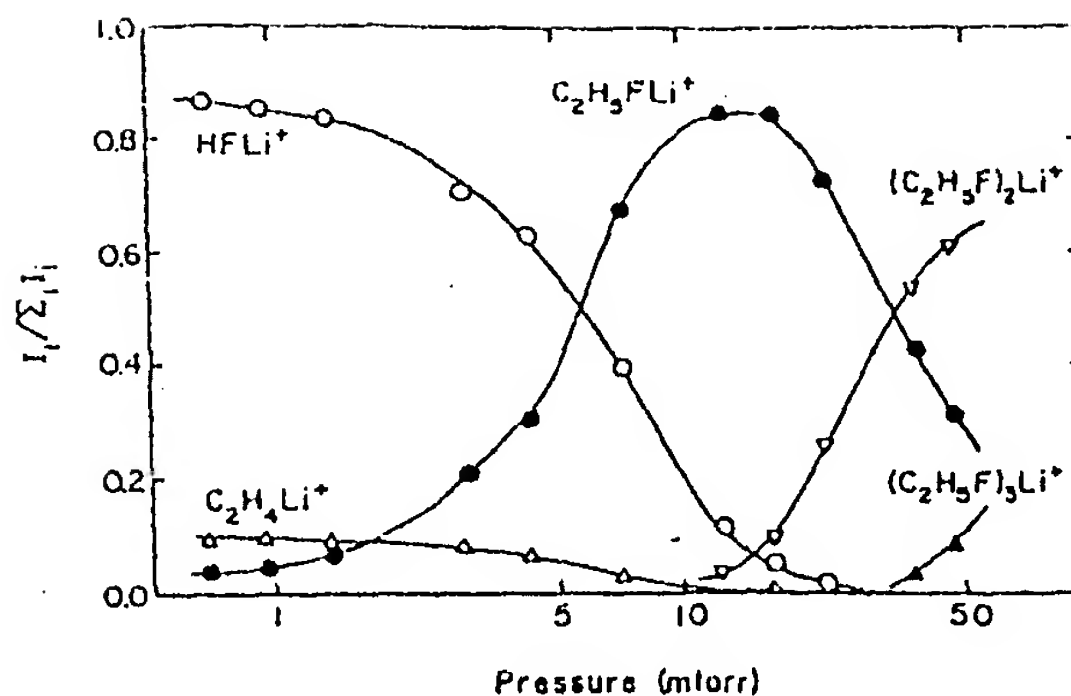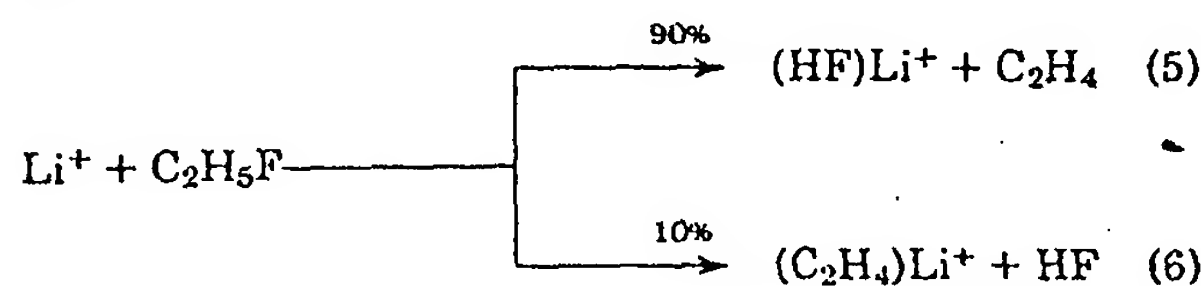

Figure 3. Variation with C_2H_5F pressure of the relative ion abundances of the products of the reaction of Li^+ with C_2H_5F

so that the transfer reactions will be exothermic. 2) In the event that direct clustering reactions are involved, the reagent gas should have a high termolecular association rate constant for the formation of reagent Li^+ complexes to maximize sensitivity. 3) The reagent gas should have a minimal tendency to cluster.

With these considerations in mind, an inert gas, N_2, and several reagent gases, including C_2H_5F and a variety of hydrocarbon species, were investigated for use in Li^+ CI mass spectrometry.

Additives in N_2. A Li^+–benzene complex was observed in the mass spectrum when N_2 with 0.5% benzene added was allowed into the reaction chamber at pressures from 20 to 50 mTorr. A Li^+ beam energy of 1 eV and an extraction potential of 5 V were used. Attempts to detect 0.1% and less of benzene in N_2 failed. No complexes of N_2 with Li^+ were detected. The role of N_2 is probably to thermalize Li^+, with scattered Li^+ then forming complexes with additives in termolecular association reactions.

Additives in C_2H_5F. The relative product ion intensities in the reaction of C_2H_5F with Li^+ are plotted as a function of C_2H_5F pressure in Figure 3. Lithium ions were injected into the chamber with an energy of 2 eV. A 5-V extraction voltage was applied across the chamber. Dehydrohalogenation of C_2H_5F occurs to give Li^+ bound to HF or C_2H_4 (Equations 5 and 6). As the pressure is increased, these species transfer Li^+ to C_2H_5F (Equations 7 and 8). At the highest pressures employed, cluster products are observed (Equation 9, $n = 1, 2$).

$$Li^+ + C_2H_5F \begin{cases} \xrightarrow{90\%} (HF)Li^+ + C_2H_4 & (5) \\ \\ \xrightarrow{10\%} (C_2H_4)Li^+ + HF & (6) \end{cases}$$

$$(HF)Li^+ + C_2H_5F \rightarrow (C_2H_5F)Li^+ + HF \quad (7)$$

$$(C_2H_4)Li^+ + C_2H_5F \rightarrow (C_2H_5F)Li^+ + C_2H_4 \quad (8)$$

$$(C_2H_5F)_nLi^+ + C_2H_5F \rightarrow (C_2H_5F)_{n+1}Li^+ \quad (9)$$

When C_2H_5F with 200 ppm of benzene added is allowed into the reaction chamber at pressures from 10–40 mTorr, the Li^+–benzene complex appears in the mass spectrum. At the higher pressures, a cluster of C_2H_5F with the Li^+–benzene complex appears. The clusters add undesirable complications to the identification of the sample composition.

Additives in Hydrocarbons. At the pressures employed in this instrument (1–50 mTorr) termolecular association reactions of Li^+ with hydrocarbons are significant. For example, benzene (Figure 4) and isobutane (Figure 5) react
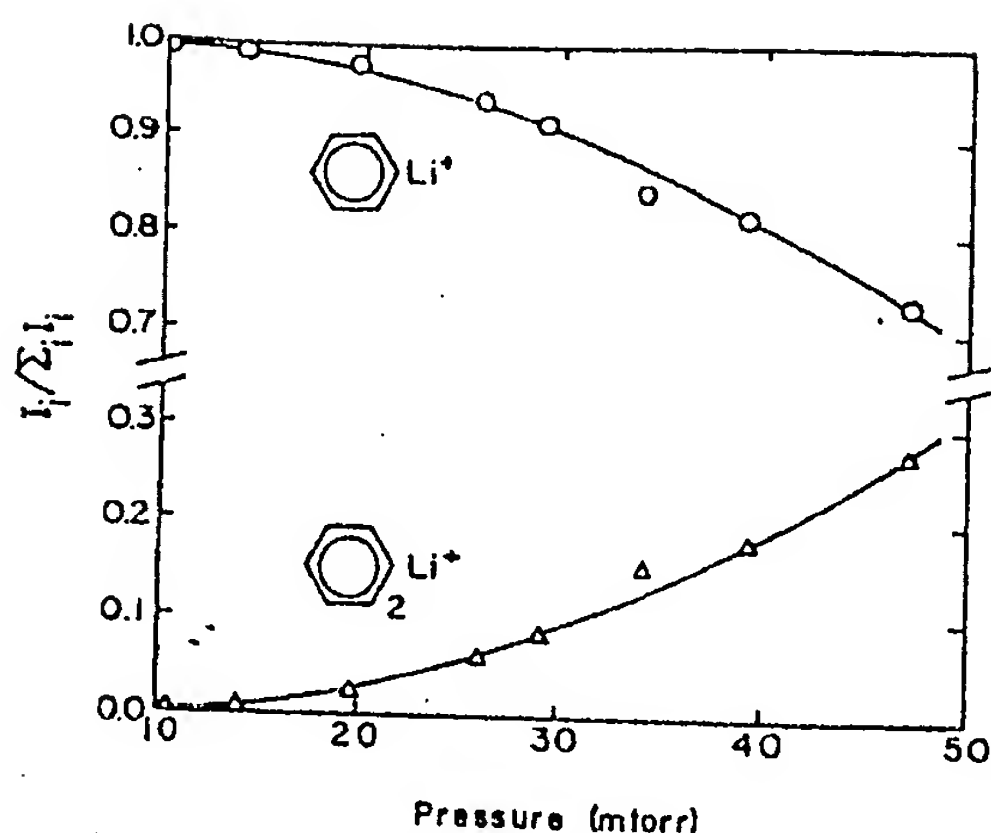
Figure 4. Variation with benzene pressure of the relative ion abundances of the products of the reaction of Li^+ with benzene
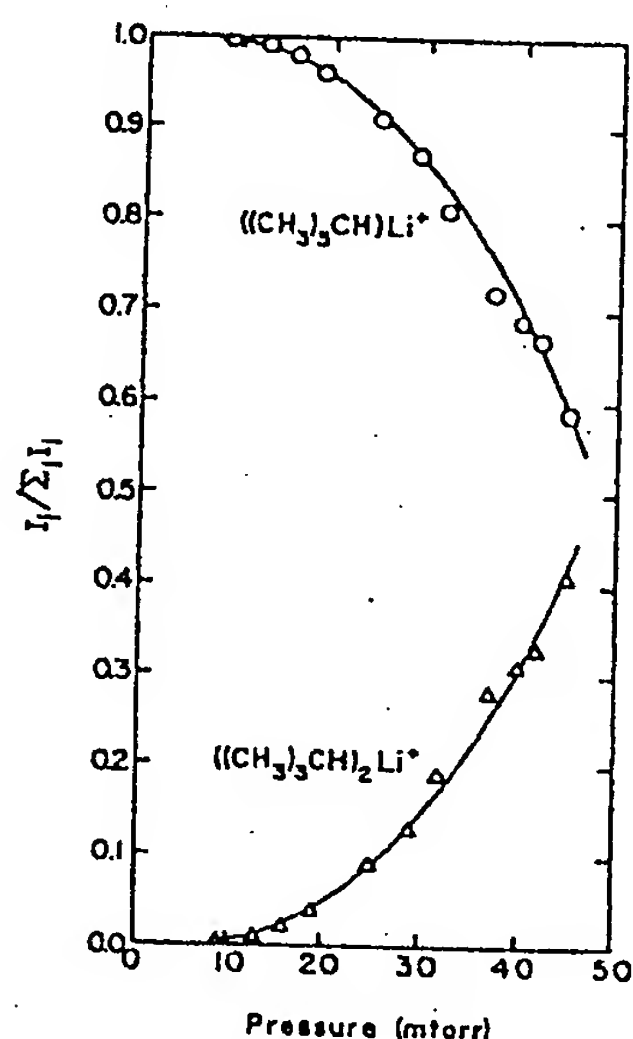

Figure 6. Li^+CI mass spectrum of a mixture of C_2H_5F, FCHCHF, $CH_3CHC(CH_3)_2$, benzene, 1-hexene, and toluene at approximately 0.1% each in isobutane. The Li^+–isobutane peak has been reduced by a factor of 200

Figure 5. Variation with isobutane pressure of the relative ion abundances of the products of the reaction of Li^+ with isobutane

with Li^+ to form an adduct with these molecules. As the pressure increases, formation of a dimer complex is observed. Cyclohexane and other saturated hydrocarbons behave similarly.

Our experience indicates that hydrocarbon species such as isobutane and cyclohexane are the best suited reagent gases for use in Li^+ CI mass spectrometry. Alkanes have a lower Li^+ binding energy than most other compounds (Figure 1) and will transfer Li^+ to a trace quantity of virtually any other compound present. The binding energy of Li^+ to cyclohexane is 24 kcal/mol (Figure 1). The binding energy to isobutane has not been determined. A value of 20 ± 5 kcal/mol is estimated based on observed trends. In addition, alkanes have a lower tendency to cluster than more polar molecules, such as C_2H_5F. The mass spectrum obtained from a mixture of six compounds in isobutane is shown in Figure 6. The six sample compounds are present at a concentration of about 0.1% each. Only the quasi-molecular species, the Li^+ complexes, are present. This is especially significant in the case of C_2H_5F, which fragments (Equations 5 and 6), when interacting with an uncomplexed Li^+. The pressure at which this spectrum was taken, 10 mTorr, is much lower than the pressure in conventional CI mass spectrometry, which is typically about 1 Torr. The low pressure is employed here to avoid cluster formation,
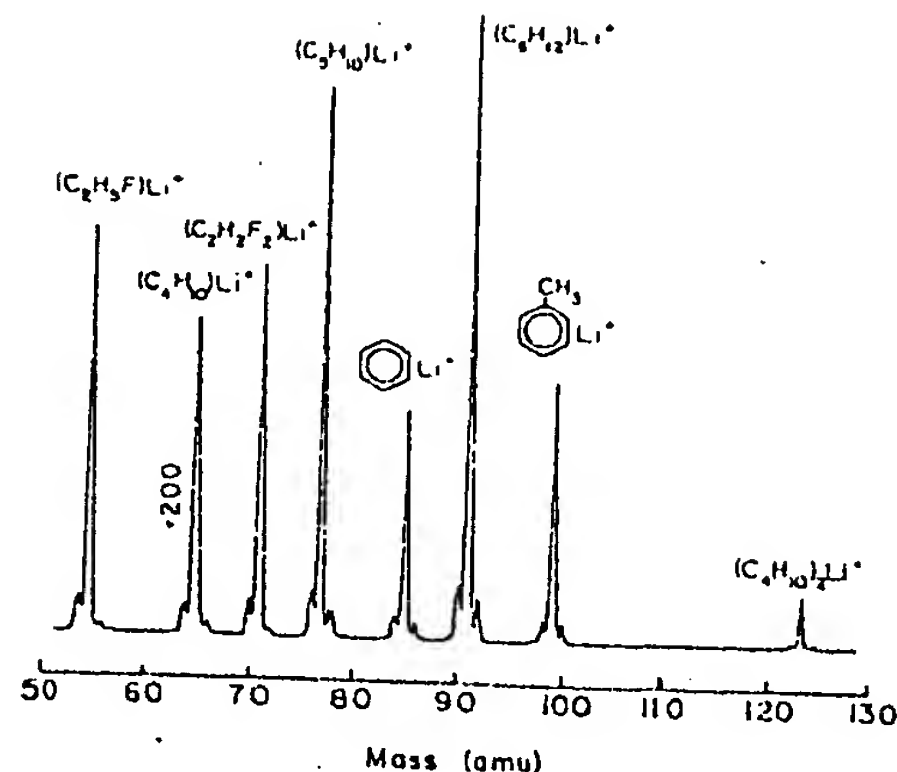
which becomes significant at higher pressures. In addition, the low pressure permits penetration of the low energy (1 eV) Li^+ beam into the chamber.

Applications. Alkali ion CI mass spectrometry is a useful addition to the field of analytical mass spectrometry. Several unique applications of Li^+ CI mass spectrometry can be envisioned. For example, it can be used to detect a trace amount of alkene in the presence of the corresponding alkane. We observed a trace amount of propene when 10 mTorr of propane was admitted into the reaction chamber. Analysis by gas chromatography confirmed the presence of 0.05% propene in the sample. Such an analysis using conventional CI mass spectrometry with methane or isobutane as the reagent gas would be difficult, since the principal ions formed in both alkanes and alkenes are alkyl ions $(C_nH_{2n+1})^+$ (21). We anticipate that alkali ion chemical ionization mass spectrometry will find numerous applications in the analysis of mixtures, with the specific procedure to be employed depending on the nature of the sample.

No attempt was made in the present study to determine the ultimate sensitivity of alkali ion CI mass spectrometry. With the present apparatus, sample molecules can be detected at the part-per-million level. The major background signal originates from scattered alkali ions which reach the multiplier. By avoiding this difficulty and employing ion counting, it is likely that the sensitivity could be extended considerably.

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hemical Ionization Mass Spectrometry of Chromium Tris-1,1,1-trifluoro-2,4-pentanedionate and Other Transition Metal -Diketonates

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chemical ionization mass spectra for the following che-
es are reported: manganese bisacetylacetonate (Mn-
ac)₂), Ni(acac)₂, Cu(acac)₂, Zn(acac)₂, Cr(acac)₃, Fe-
ac)₃, Co(acac)₃, Ru(acac)₃, Rh(acac)₃, manganese
-1,1,1-trifluoro-2,4-pentanedionate (Mn(tfa)₂), Ni(tfa)₂,
tfa)₂, Zn(tfa)₂, VO(tfa)₂, Cr(tfa)₃, Fe(tfa)₃, Co(tfa)₃,
tfa)₃, Rh(tfa)₃, nickel bis-1,1,7,7-tetramethyl-4,6-hep-
edionate (Ni(thd)₂), Cu(thd)₂, Zn(thd)₂, VO(thd)₂,
thd)₃, Fe(thd)₃, Mn(thd)₃, and Co(thd)₃. Also a system
escribed whereby solutions can be injected directly into
ionization source of a chemical ionization mass spec-
neter (CIMS). Preliminary detection limits of 1 part per
on (ppb) for Cr(tfa)₃ in toluene were obtained with the
ct injection system.

he natural abundance of chromium in igneous rocks in
form of chromite is of the order of 0.02%, and soils have
n found to contain from traces to 2.4% of chromium. As
irect result of this natural level of chromium, most
its contain chromium in the range of 100–500 mg/kg of
matter. Chromium is used industrially in the following
ducts or processes: alloys, plating, catalysts, tanning,
nts, mordants, and fungicides. The average total daily
ake of 30–40 mg of chromium by man is derived from
following sources: food (30–100 mg), water (0–40 mg),
air (0.3 mg). This quantity of chromium more than
sfies this essential trace element requirement, since
omium III is known to be involved in carbohydrate and
metabolism. As a result, excess dietary chromium is ex-
ed in the feces and some of the absorbed chromium is
irned to the intestinal tract in bile or excreted in the
1e. Traces of chromium have been thought to be stored
n insoluble form in the lungs (1).
arious studies have been made in order to ascertain the
c effects of exposure to chromium. It has been observed
t the skin, nasal membrane, lungs and kidneys can be
e prone to carcinomas with high levels of chromium
3). As a result of this interest in low-level concentra-
s of chromium, extensive use of electron impact (EI)
s spectrometry has been made via complexation with

β-diketones (9–20). All these analyses used the Cr(β-dike-
tonate)₂⁺ ion which is the base peak in the EI mass spec-
trum.

Recent studies have shown that chemical ionization mass
spectrometry (CIMS) for trace metal analysis is attractive
because the resulting mass spectra are simple (21, 22). This
present paper is intended to show the analytical applica-
tion of CIMS for the analysis of chromium β-diketonates
by direct injection of solutions of chromium tris-1,1,1-tri-
fluoro-2,4-pentanedionate (Cr(tfa)₃) in toluene into the
source of the CI mass spectrometer. Also the mass spectra
of a series of other metal chelates are reported.

EXPERIMENTAL

Chelate Preparation. The 2,4-pentanedionates (acac), the
1,1,1-trifluoro-2,4-pentanedionates (tfa), and the 2,2,6,6-tetra-
methyl-3,5-heptanedionates (thd) of VO(II), Cr(II), Mn(II),
Mn(III), Fe(III), Co(III), Ni(II), Cu(II), Zn(II), Ru(III) and Rh(III)
were prepared by methods which have been described previously
(23, 24).

Apparatus. The CI mass spectra were obtained using a scientif-
ic Research Instruments Corporation BIOSPECT system with ei-
ther isobutane or methane as the reagent gas, which has been de-
scribed previously (21, 22). Aliquots of known solutions of the
metal chelates in toluene were evaporated onto the direct insertion
probe, and the probe was inserted directly into the ionization
source. The following are the source temperatures used to sublime
the chelates into the mass spectrometer: 130–180 °C (acac), 130 °C
(tfa), and 130 °C (thd). All other conditions were identical with
those previously reported (21). The mass-to-charge ratios of the
various peaks in the mass spectra were determined by the mass
marker which has been calibrated with methyl stearate.

The sensitivity studies for Cr(tfa)₃ were made in the following
manner: the quadrupole mass filter was tuned to unit resolution in
the region of the protonated molecular ion [Cr(tfa)₃H⁺] (512 amu)
and then it was set to repeatedly scan the mass region 507 to 517
amu in 200 ms.

RESULTS AND DISCUSSIONS

CI Mass Spectra. In order that the CI mass spectra
could be interpreted, a similar computation of relative in-
tensities as has been reported previously (21) was per-
formed, and the results are summarized in Tables I–III.
These results are based on the contributions due to the
natural isotopic abundances of the metal isotopes, H^2, C^{13},